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Electrochemical and Adsorption Properties of Catalytically Formed Carbon Nanofibers

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1. Introduction

After the development of high resolution electron microscopy, the carbon structures of nano dimensions could be explained and investigated in detail and have been used in many fields. These different nanoscale carbon structures have remarkable and unique chemical, physical and mechanical properties.

Carbon has long been known to exist as amorphous carbon and in two crystalline allotropic forms: graphite and diamond. Many other carbon based nanomaterials have been developed: fullerenes-discovered by Kroto et al., 1985; carbon nanotubes (CNTs): multi-wall carbon nanotubes (MWCNTs)-recognized discovery attributed to Iijima, 1991 and single-wall carbon nanotubes (SWCNTs) reported at the same time by Iijima & Ichihashi, 1993 and Bethune et al., 1993. The article by Iijima, 1991 which showed that carbon nanotubes were formed during arc-discharge synthesis of C₆₀, has also brought a great interest for carbon nanofibers (CNFs).

The history of carbon nanofibers (nanofibers and nanotubes) also named nanofilaments, goes back in the 19th century. A method for growth of catalytically carbon filaments using iron catalyst and a carbon source gas was first patented by Hughes & Chambers, 1889.

Radushkevich & Lukyanovich, 1952 obtained hollow graphitic carbon fibers that were 50 nanometers in diameter. They were the first who mentioned *carbon nanofibers*, but for a long time these nanostructures were of no industrial importance (Peshnev et al., 2007).

The interest in the structure of these filaments and their properties emerged in the 1970s with the development of transmission electron microscopy, when the proposal of growth mechanism of Oberlin et al., 1976 was reported. They grew nanometer-scale carbon fibers by chemical vapour deposition (CVD). Tennent, 1987, presented a U.S. patent for graphitic, hollow core "fibrils".

The recent increasing scientific and industrial interest in carbon nanofilaments as one-dimensional nanomaterials, originates from their unusual application properties and similarities with carbon nanotubes.

Carbon nanofibers have been extensively studied: their synthesis and growth mechanism (Oberlin et al., 1976; Tibbetts et al., 1993, 1994; De Jong & Geus, 2000; Helveg et al., 2004; Cui et al., 2004a), their structure (Endo et al., 2002, 2003; Paredes et al., 2005; Eksioglu & Nadarajah, 2006; Lawrence et al., 2008;) and properties (Endo et al., 1993, 1995; Kavan & Dunsch, 2008; Charlier et al., 2008; Damnjanovic et al., 2005). CNFs have been recognized as a very promising material based on their nanostructure and properties.

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In this chapter we focus on the electrochemical and adsorption properties of carbon nanofibers prepared by catalytic chemical vapour deposition (CCVD) method, underlying the results obtained by the authors.

We first present some of up to date literature concerning the CVD synthesis of CNFs. Thereafter, we resume the electrochemical and adsorption properties of the as prepared CNFs and we also show our own results. Our studies have evidenced that among all carbon nanostructures prepared by us, carbon nanofibers showed the best electrochemical characteristics. As a consequence, CNFs were successfully used as support for biologically active substances (amino acids, glucose oxidase, DNA). The application of nanofibers in the sensors area was also described. CNFs prepared by CCVD method have been successfully used for the construction of second-generation glucose biosensors. The enzyme and the redox mediator were easily co-immobilized on the surface of carbon nanofibers due to its high specific area. The linear response range of this glucose biosensor was between 1.7 and 7mM while the time required to reach 95% of the steady state, was around 30 seconds. We have used in an original manner an amperometric method to detect the changes in the specific activity of GOx, immobilized longer time on CNFs.

Finally, we summarize issues with respect to the research goals to be dealt with, in future work.

2. Application fields of carbon nanofibers

The application area of CNFs depends very much on the synthesis conditions, which strongly influence the properties of these nanostructures.

CNFs are the subject of extensive experimental and theoretical studies for specific applications, such as: adsorbent (including hydrogen storage material for fuel cells, lithium-ion secondary batteries and supercapacitors), catalysts or catalyst supports, polymer additives, template for fabrication of various nanostructures (Ju et al., 2008; Van der Lee et al., 2005; Kymakis & Amaratunga, 2002; Li et al, 2006). CNFs are of great interest for the development of nanoelectronics components (field effect transistors, diodes, electrochemical capacitors, electron sources) or analytical sensors (Baughman et al, 2002; Liu & Hu, 2002).

Carbon nanostructures such as vertically aligned carbon nanofibers (VACNFs) and nanocones produced by plasma enhanced CVD (PECVD) are nanomaterials of great interest due to their potential applications in areas such as: tips for scanning microscopy (Cui et al., 2004 b), field-emission devices (Fan et al., 1999), biological probes (Guillorn et al., 2002), interconnects for nanoelectronics and memory devices (Grobert et al., 1999). The incorporation of VACNFs as a nanostructured material into multiscale devices has often enhanced the performance of the combined system (Baker et al., 2005). Trace analysis and DNA hybridization detection with VACNF electrodes have been demonstrated by Koehne et al., 2004. Nanofiber arrays have been incorporated as vertically oriented diffusion barriers in microfluidic devices, to mimic cell functionality (Fletcher et al., 2004). The high aspect ratio and mechanical stability of VACNFs has also been proved useful for the parallel delivery of molecular species, including DNA, cells and tissues (McKnight et al., 2004).

The interest in nanosystems for biological applications is continuously growing, especially for fabrication of nanosensors, molecular probes, miniaturized biomedical devices and bioreactors (Huang et al., 2002; Hu et al., 2004; Brown et al., 2008). The adsorption of biological molecules on different carbon nanostructures may offer the possibility of

fabricating biosensors on a nanometer scale. Applications of nanotubes such as drug delivery into a single cell have been referred to (Kam et al., 2004).

Efficient adsorbents research for enzymes and microorganisms are very important for development of modern bioprocesses of hydrolysis, oxidation and isomerization. Highly stable heterogeneous biocatalysts were prepared by immobilization of enzymatic active substances on inorganic supports (enzymes-in particular glucoamylase; intracellular compartments and whole cells of microorganisms) (Kovalenko et al., 2009 a).

Multiple and specific applications require optimum preparation methods of CNFs. It is very important to identify and control the critical parameters for the optimization of the synthesis process and the application of nanocarbon products.

3. Synthesis methods of carbon nanofibers

Carbon nanofilaments have been synthesized by various methods, for example laser vapourization (Baker et al., 1997), arc discharge (Iijima, 1991), catalytic chemical vapour deposition (Zheng et al., 2004) and plasma-enhanced chemical vapour deposition. Several PECVD methods developed by Ren et al., 1999 have been used for growth of nanofibers, including microwave discharges (Woo et al., 2002), direct current (dc) or radio frequency (rf) glow discharges (Merkulov et al., 2002) and inductively coupled discharges (Delzeit et al., 2002).

Catalytic Chemical Vapour Deposition (CCVD) method

The most developed method for the synthesis of CNFs is CCVD method. The advantage of the method consists in the possibility to control the morphology and structure of nanocarbon products, to improve the alignment of nanofilaments and to obtain large amounts with high purity and low costs for all kind of applications. A variety of CVD processes have been used for carbon nanofilaments synthesis, which include catalytic thermal CVD, plasma-enhanced CVD, alcohol catalytic CVD, aerogel-supported CVD, laser-assisted CVD (Govindaraj & Rao, 2006) and thermal gradient CVD (Ling-Jun et al., 2009). Lower temperature for CNFs growth using heterogeneous metal catalysts, was suggested by other researchers (Poirier et al., 2001).

There are numerous experimental parameters that can be adjusted during the synthesis process of CNFs, by CCVD. By selecting the metal catalyst, carbon precursors (sources) and reaction conditions (thermal energy) one can control the structure, morphology and their relating properties. Therefore, right combination of these three components makes it possible to selectively synthesize various types of carbon nanofilaments, ranging from SWCNTs and MWCNTs to CNFs.

The synthesis of carbon nanofilaments by CCVD method is based on the catalytic decomposition of a gaseous or volatile compound of carbon source (methane, carbon monoxide or acetylene, C_2H_4 , methanol/ethanol, benzene (Devaux et al., 2009), on a variety of transition metals (usually iron, cobalt, nickel and their alloys; palladium is rarely employed as a catalyst for solid carbon deposition-Atwater, et. al., 2009), either in a powdered or supported form as the catalytic entities (which also serve as nucleation sites for the initiation of nanocarbon growth), over the temperature range 400-1000°C. The carrier gas is argon, hydrogen, nitrogen. Sometimes hydrogen is added to reduce the metallic oxides to metal.

Lupu et al., 2004a used the CCVD method in which the outer furnace was replaced by a high frequency induction heating. Various types of CNFs were obtained by using different

catalysts. This mode combined with the CCVD method allows a significant decrease of energy consumption and a shorter reaction time as compared with the heating mode with outer furnace. CNFs have been synthesized by decomposition of pure ethylene over Fe:Ni:Cu catalyst in a horizontal furnace. The catalyst was prepared from nitrate solutions by co-precipitation with ammonium bicarbonate and was calcined at 400° C for 4 h. The carbonaceous products were purified by extraction in HCl (37%) for 24 h, washed with distilled water, and dried at 150°C for 3 h. A typical transmission electron microscope (TEM) image (Figure 1) of the sample shows nanofibers with “herringbone” structure and diameters ranging from 80 to 290 nm, similar to those reported in the literature. Their specific area was determined by the BET method and the value was between 170-242 m²g⁻¹. The CNFs have been characterized by cyclic voltammetry and their adsorption properties for biologically active substances have been closely followed (Pruneanu et al., 2006; Olenic et al., 2009).

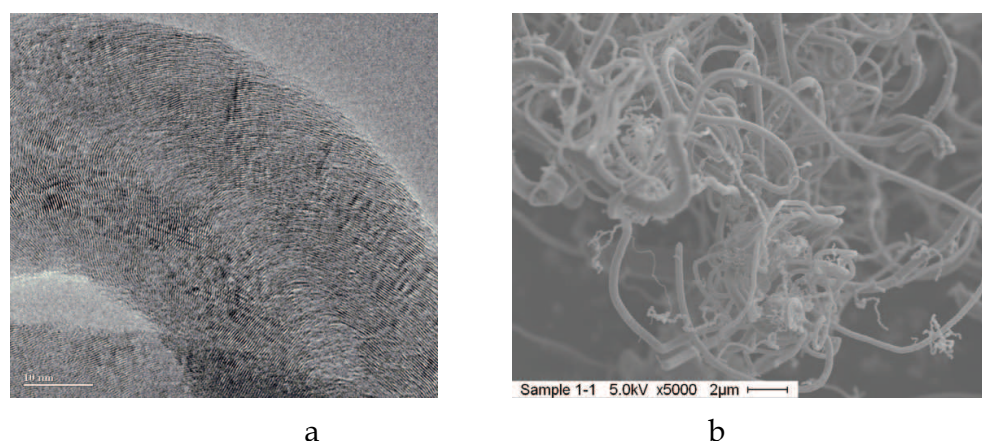


Fig. 1. (a) HRTEM image of CNF (from ethylene at 600° C on Fe:Ni:Cu as catalyst); (b) SEM image of CNFs. Reprinted from ref. Olenic et al., 2009 with kind permission of Springer Science and Business Media.

In the synthesis of nanocarbon structures by CCVD method, the critical step is the catalyst preparation. Metal nanoparticles catalyst (optimum size between 0.4-5 nm) favours the catalytic decomposition of the carbon source gas in a temperature range of 600-1100° C. As was shown in the literature, the amorphous carbon is deposited from the thermal decomposition (pyrolysis) of the carbon source gas, whereas the carbon nanofibers are grown from the catalytic decomposition of the carbon source gas (Teo et al., 2003).

According to the growth procedure, CVD method includes the seeded catalyst method (Li et al., 1996) which uses the catalyst seeded on a substrate within a reactor (in this case the interactions between the catalyst and support (alumina, silica, silicon) dictates the growth mode (Randall et al., 2001); an advantageous one is the floating catalyst method which is a method wherein the carbon vapour and the catalytic metal particles both get deposited in the reaction chamber, without a substrate. (Martin-Gullon et al., 2006).

One of the CVD methods that has been developed is the synthesis of vertically aligned nanofibers bundles for specific applications. The synthesis of VACNFs arrays were all carried out in horizontal reactors (Cao et al., 2001). All the reported products by vertical floating catalyst method were randomly arranged CNFs (Perez-Cabero et al., 2003). There are few reports on aligned CNF bundles synthesized by floating catalyst procedure, in vertical reactors (Cheng et al, 2004).

VACNFs were also obtained by low-pressure inductively coupled PECVD (Caughman et al., 2003); isolated VACNFs were synthesized by Melechko et al., 2003.

When CNFs are prepared, crystallized structures are generally desired (amorphous carbon-free). The growth temperature affects the crystallinity: a too high temperature leads to the formation of pyrolytic amorphous carbon. This is the reason for preferring the highest deposition temperature without significant self-decomposition of the carbon source gas.

The growth mechanism leading to the formation of CNFs (reviewed by Teo et al., 2003) has been studied by many groups. Baker et al., 1972 proposed a growth mechanism for both nanofibers and nanotubes, which was later completed. Other models for growing CNFs were proposed by Oberlin et al., 1976, Koch et al., 1985, Zheng et al., 2004. Formation mechanism of large branched carbon nano-structures has been presented by Devaux et al., 2009.

Examination of synthesized CNFs by TEM and SEM reveals the basic microstructure of graphitic CNFs. There are two types of carbon nanotubes: single-wall and multi-wall and four types of carbon nanofibers that consist of stacked graphite layers, which can be arranged parallel (tubular-adopting the structure of a “multi-walled faceted nanotube”), perpendicular to the fiber axis (platelet-adopting the arrangement of a “deck of cards”), or herringbone structure (the graphite platelets are at a particular angle to the fiber axis), and amorphous type without crystalline structure. Most of carbon nanofibers and nanotubes synthesized by CCVD method are crystalline or partially crystalline and only a few of them are amorphous.

The herringbone structure seems to be favoured when the catalyst is an alloy. Herringbone-type CNFs with large diameter and a very small or completely hollow core have been synthesized through a CVD method (Terrones et al., 2001).

The only difference among the various forms of carbon nanofilaments is their chemical structure. Martin-Gullon, et al., 2006, present in detail a classification of nanofilaments depending on their structure.

The properties related to the morphology of CNFs depend on many factors, like: the chemical nature of the catalyst and the conditions of its pretreatment (Huang et al., 2009; Kovalenko et al., 2009 b), the composition and flow rate of a gas mixture and the temperature and duration of the synthesis (Endo et al., 2003; Chuang et al., 2008).

On the other hand, the electrical and optical properties of carbon nanostructures are largely dependent on their structures (Kataura et al., 1999; Yang et al., 2003).

The conducting properties of CNFs that can be varied from metal to semiconductor (depending on the structural parameters and doping with heteroatoms) are very important for practical applications (Ismagilov, 2009).

All CNFs products obtained by CCVD method contain impurities such as metal catalyst particles, amorphous carbon and carbon nanoparticles depending on the reaction conditions. Therefore, purification of carbon nanostructures is of great importance for technological applications.

A purification step is usually required before carbon nanofilaments can be used, especially for biomedical applications. Several purification methods are reported in the literature (Liu et al., 2007). Graphitization (or heat treatment) is one of the most effective methods to remove defects or impurities such as metallic compounds, which diminish the electrical and mechanical properties of conventional carbon nanofibers.

Huang et al., 2009 demonstrated that high purity CNFs can be formed by varying the synthesis temperature. Different types of CNFs were characterized by various techniques to understand their crystal structure, morphology, graphitization degree and thermal stability.

For more complex applications of carbon nanotubes, different functionalization methods have been introduced. Investigation of the interaction between carbon nanotubes and biological molecules are very important (Zhong et al., 2009).

McKnight et al., 2006 showed several approaches toward such site-specific functionalization along the nanofiber length, including physical and electrochemical coating techniques, chemical immobilization of DNA and enzyme species, and covalent attachment of biotin followed by affinity-based capture of streptavidin-conjugated molecules.

4. Electrochemical properties of carbon nanofibers

For many electrochemical applications, carbon is a well known material of choice. Among its practical advantages are: a wide potential window in aqueous solution, low background current, lack of corrosion processes at positive potentials and low costs.

The advantages of CNFs in the construction of biosensors, relate to their small size with large specific area, the promotion of electron transfer when used in electrochemical reactions and easy bio-molecules immobilization. DNA molecules can be covalently bound on the functionalized fiber surface (e.g. with carboxylic groups). In comparison with the classical carbon electrodes, CNFs show better electrodic behaviour including good conducting ability and high chemical stability. The electrochemical properties of CNFs paste electrodes have been largely studied. In most cases, CNFs were prepared as composite electrodes.

It is of interest to explore the properties of carbon nanocomposite electrodes to see if they might exhibit new properties, due to the high edge/surface area ratio of such materials.

Marken et al., 2001 have evaluated CNFs (obtained by ambient pressure CVD method) as novel electrode materials for electrochemical applications (porous, pressed onto a glassy-carbon substrate and non-porous, embedded in a solid paraffin matrix). They exhibit low BET surface areas and high electrochemical capacitances due to the fact that the spaces between the fibers allow the penetration of electrolyte solution. Capacitive currents tend to mask voltammetric currents during cyclic voltammetry. By comparison, when the spaces between CNFs are impregnated by an inert dielectric material (paraffin wax) the electrode has good conductivity and low capacitance. These materials were compared with other forms of nanostructured carbons: aerogel or activated charcoal.

Van Dijk et al 2001 prepared nanocomposite electrodes made of CNFs and black wax and used them for anodic stripping voltammetry of zinc and lead.

Maldonado et al., 2005 have prepared nondoped and nitrogen-doped (N-doped) CNFs films by the floating catalyst CVD method using precursors consisting of ferrocene and either xylene or pyridine to control the nitrogen content. CNF coated nickel-mesh was used as working electrode, to study the influence of nitrogen doping on the oxygen reduction reaction. The electrodes have significant catalytic activity for oxygen reduction in aqueous solutions (neutral to basic pH).

Yeo-Heung et al., 2006 tested the electrochemical actuation properties of carbon nanofiber-polymethylmethacrylate (CNF-PMMA) composite material. They characterized the CNF-PMMA actuator by impedance spectroscopy, at voltages up to 15V. The relationship between displacement and applied voltage was determined.

Roziecka et al., 2006 prepared ITO electrodes modified with hydrophobic CNFs-silica film, which was employed as support for liquid/liquid redox systems. The redox processes within the ionic liquid is coupled to ionic transfer processes at the ionic liquid/water

interface. Therefore, the CNFs electrode material was an excellent support for recording both the Faradaic and capacitive currents. The efficiency of the electrode process increases due to the use of the heterogeneous matrix.

Our group has studied the electrochemical properties of carbon nanofilaments (CNFs, MWCNTs and SWCNTs- unpublished data). Paste electrodes were prepared by mixing the carbon powder with silicon oil and then packing the resulting paste into the cavity of a PVC syringe (2.5 mm diameter). The electrical contact was ensured by a Pt wire, tightly inserted into the paste.

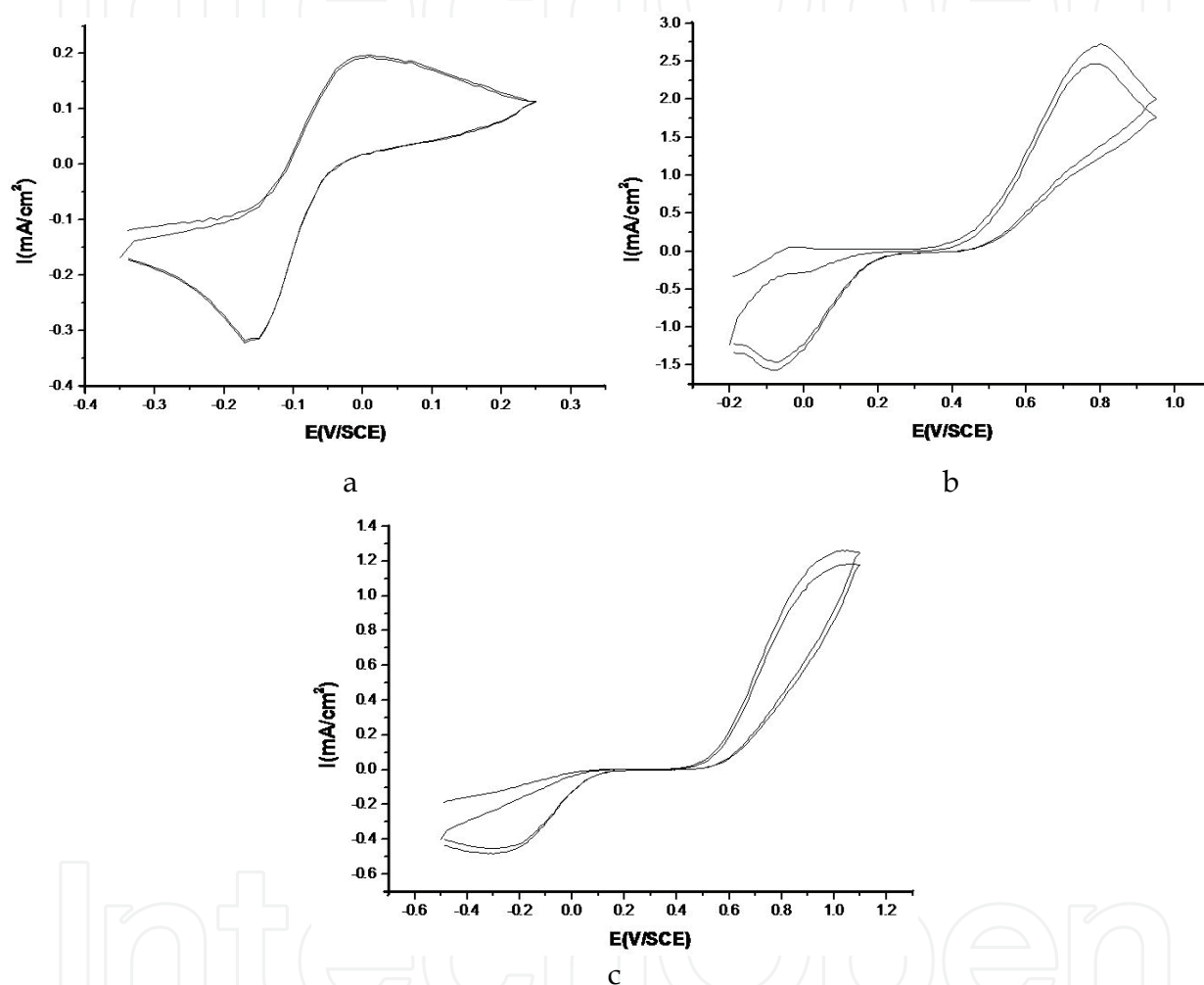


Fig. 2. Cyclic voltammograms recorded in solution of 10^{-2} M hydroquinone and 0.5M KCl for: a) CNFs; b) MWCNTs; c) SWCNTs paste electrode; all voltammograms were recorded with a sweep rate of 100 mVs⁻¹.

The electrochemical behaviour of these types of electrodes was investigated by cyclic voltammetry (100 mVs⁻¹ sweep rate) using as redox mediator a solution of 10^{-2} M hydroquinone (Figure 2 a,b,c). From Figure 2a one can see that carbon nanofibers showed the best electrodic properties. The voltammograms exhibit two well-defined peaks, with the peak potential separation, ΔE_p , around 150 mV. This value is higher than that generally obtained for a reversible redox system ($60 \text{ mV}/n$, where n is the number of electrons transferred during the reaction).

For MWCNTs and SWCNTs paste electrode, the peak potential separation, ΔE_p is considerable larger (850 mV and respectively 1100 mV), indicating a lower conductivity and a slow transfer of electrons.

Due to the excellent electrodic properties of CNFs paste electrode, Pruneanu et al., 2006 have studied the oxidation of calf thymus DNA. The interest in this kind of research is due to the fact that the electrochemical oxidation may mimic the biological oxidation mechanism, involving enzymes. All the four bases of DNA can be chemically oxidized; electrochemically, only guanine and adenine oxidation peaks can be recorded (thymine and cytosine have oxidation potentials larger than 1.2V vs. Ag/AgCl). In order to establish the exact position of purine oxidation potentials (adenine and guanine) the authors have registered differential pulse voltammetry (DPV) curves, in solution containing 10^{-3} M adenine hemisulphate and 10^{-3} M guanine hemisulphate (in 0.1M PBS pH 7+ 0.5M KCl, Figure 3). The two peaks that appeared around 0.9V vs. Ag/AgCl and 1.18V vs. Ag/AgCl were ascribed to guanine and adenine oxidation, respectively. The intensity of the peaks decreased after successive recordings, due to the irreversible character of the oxidation process.

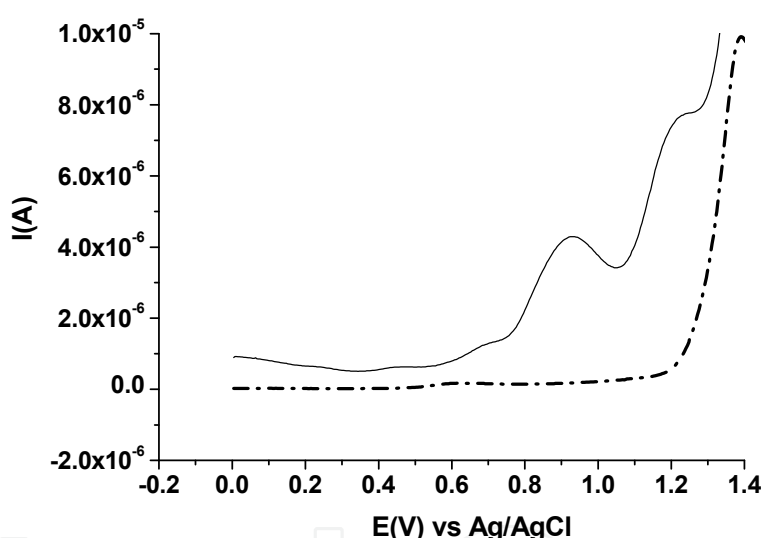


Fig. 3. DPVs recorded in a solution of 10^{-3} M adenine hemisulphate and 10^{-3} M guanine hemisulphate, in 0.1M PBS (pH 7) + 0.5M KCl.

The signals obtained from guanine or adenine oxidation can be used for the construction of a DNA biosensor. In Figure 4 one can see that the oxidation peak of adenine hemisulphate increases with the increase of solution concentration (10^{-7} 10^{-3} M).

Oxidation of calf thymus DNA (single stranded or double stranded DNA) at carbon nanofibers paste electrode was also studied by DPV (Figure 5). Prior experiments, calf thymus DNA was physically adsorbed on the electrode surface, by immersing it in DNA solution for about five minutes, under constant stirring. The two peaks corresponding to guanine and adenine oxidation were clearly recorded for single stranded DNA (Figure 5, straight line). In contrast, no signal was obtained when double stranded DNA was adsorbed at the electrode surface (Figure 5, dashed line). This may be explained by the fact that in

double stranded DNA the purine bases are hidden between the double helix, so they have no free access to the electrode surface. In this case the transfer of electrons cannot take place.

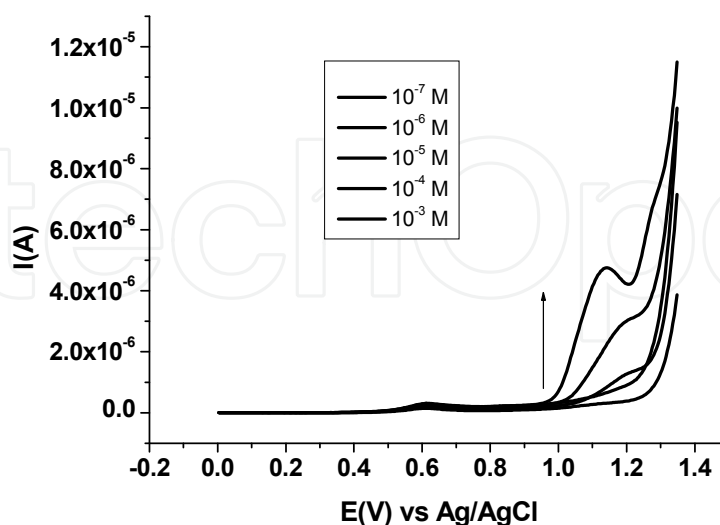


Fig. 4. DPVs recorded in solutions of adenine hemisulphate of different concentration: 10^{-7} 10^{-3} M in 0.1M PBS (pH 7) + 0.5M KCl.

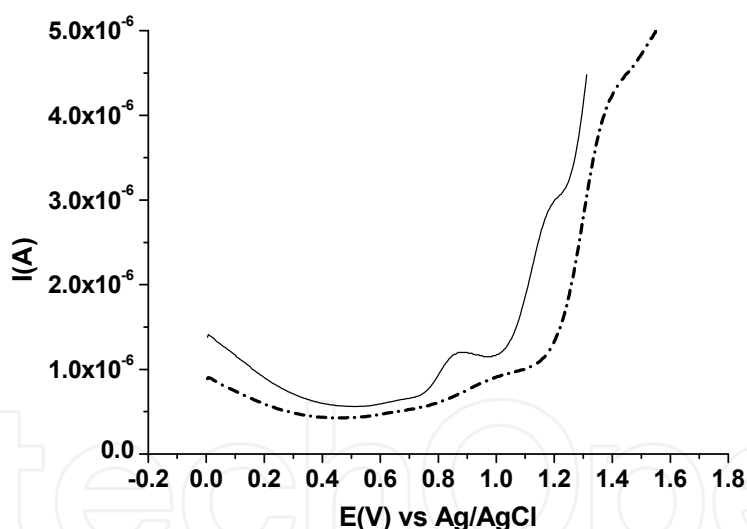


Fig. 5. DPVs of single-stranded DNA (straight line) and double-stranded DNA (dashed line) in solution of 0.1M PBS (pH 7) + 0.5M KCl (0.3 mgml^{-1} DNA)

Zhang et al., 2004 performed $I - V$ measurements on individual VACNFs. They fabricated multiple Ti/Au ohmic contacts on individual fibers, having the contact resistance of only few kOhm. The measurements demonstrated that VACNFs exhibit linear $I - V$ behaviour at room temperature. Between intergraphitic planes in VACNFs exists a dominant transport mechanism of electrons, along the length of the fiber.

VACNFs are increasingly used in bioelectrochemistry, due to the fact that they exhibit fast electron transfer to redox species from solution, or act as highly conducting substrates to

connect redox enzymes to macro-sized electrodes. Their chemical stability combined with a high degree of biologically accessible surface area and nanoscale dimension make VACNFs ideal substrates for the development of scaffolds in biological detection. Additionally, their mechanical strength and narrow diameter allow easy cell penetration, making them suitable for intracellular electrochemical detection.

Baker et al., 2006a demonstrated the ability to use VACNFs as electrodes for biological detection. He also emphasized the importance of the surface functionalization, in order to control the overall electrochemical response. Functionalized VACNFs with the redox active protein *cytochrome c* were characterized by cyclic voltammetry (CV) measurements. Although the high surface area of the nanofibers allows the *cytochrome c* molecules to produce an increase of the electrochemical current, the high capacitive currents partially obscured this signal and partially offset the potential improvement in the signal-to-noise ratio.

VACNT arrays were successfully grown on planar graphitic carbon substrates, using a bilayer Al/Fe catalyst and water-assisted thermal CVD. Excellent voltammetric characteristics were demonstrated after insulating the arrays with a dielectric material (Liu et al., 2009).

A method for the development of an amperometric biosensor for interference-free determination of glucose was reported by Jeykumari & Narayan, 2009. The bienzyme-based biosensor was constructed with toluidine blue functionalized CNTs. The electrochemical behaviour of the sensor was studied by impedance spectroscopy, cyclic voltammetry and chronoamperometry. The excellent electrocatalytic activity of the biocomposite film allowed the detection of glucose under reduced over potential, with a wider range of determination and with a very good detection limit. The sensor showed a short response time, good stability and anti-interferent ability. The proposed biosensor exhibits good analytical performance in terms of repeatability, reproducibility and shelf-life stability.

Sadowska et al., 2009, functionalized MWCNTs with azobenzene and anthraquinone residues (chemical groups with redox activity) for potential application in catalysis and memory storage devices. Using the Langmuir-Blodgett method, the nanotubes containing electroactive substituents were transferred onto electrode substrates and characterized by cyclic voltammetry. The amount of electroactive groups per mg of nanotubes was calculated based on the cathodic current peak. A highly reproducible voltammetric response was obtained with a single nanotube layer or multiple nanotube/octadecanol layers. It is believed that such devices will be invaluable for future high-performance electrodes.

Minikanti et al., 2009 designed implantable electrodes as targets for wide frequency stimulation of deep brain structures. They have demonstrated by cyclic voltammetry and impedance spectroscopy, the enhanced performance of implantable electrodes coated with multi-wall carbon nanotube. The results were compared with those obtained for the more traditional stainless steel. They also investigated the surface morphology of aged electrodes due to the fact that implantable electrodes have to be mechanically stable and present high shelf life. The effect of superficial oxygen adsorption on the aged MWCNTs electrodes was observed through a modified cyclic voltammetric spectrum.

In the past few years, considerable interest was focused on the application of carbon based nanomaterials as electrodes for supercapacitors, due to their chemical inertness and easy processability. The capacitive behaviour of the CNFs was studied in term of charge-discharge curves and cyclic voltammetry.

Recently, carbon nanomaterials with various morphologies (carbon nanotubes, nanofibers, nanowires and nanocoils) have been intensively studied as negative electrode materials in

lithium-ion batteries (Zou et al., 2006). These nanofibers have low graphitic crystallinity. The experimental results showed that CNF electrodes had high reversibility with small hysteresis, in the insertion/extraction reactions of lithium-ion.

All these studies suggest that CNFs represent a new class of materials suitable for electrochemical applications.

5. Adsorption properties of carbon nanofibers

The biologically active substances can be attached to CNFs surfaces by physical adsorption (physisorption) or chemical immobilization.

For a long time, activated carbons (ACs) materials containing large surface area and well-developed porosity were successfully applied in various industrial processes including adsorption (gases and liquids), mixture separation, filtration, etc.

CNFs and activated CNFs have special properties, compared with activated carbon. Among these, we mention the high chemical reactivity due to the large fraction of active sites, available for chemical and physical interaction with different species.

Baker, 2007 noticed the use of nanofibers as adsorbents. He additionally emphasized that the functionality of carbon nanofiber surface has an important role. The raw graphitic materials are free of surface oxygen groups and therefore are hydrophobic in nature. CNFs surface can have a hydrophilic character after a normal activation procedure. The control of the acid-base properties of carbon nanofibers surface has an important impact on a variety of potential applications. The structural characteristics e.g. the infinite number of graphite layers and the weak Van der Waals forces are responsible for the high adsorption capacity observed for these nanostructures.

Bououdina et al., 2006 presented a review on hydrogen absorbing materials. The hydrogen is theoretically adsorbed on the surface of CNFs and then incorporated between the graphitic sheets. The structure of CNFs allows the physisorption of large amounts of hydrogen. The used catalyst was unsupported NiO powder. As regarding the catalyst, they noticed that at low temperatures (400°C) Ni₃C is formed while metallic Ni is formed at high temperatures (500°C). The usage of high temperature (700°C) and Ni catalyst favour the formation of crystalline structure. The Ni₃C phase leads to the formation of herringbone structure while Ni favours the formation of platelet structure. They also noticed that at low temperature, the surface area of as-prepared CNFs increased about three times. The microstructural modifications of obtained carbon nanostructures bring great benefits, by correlating the catalytic phases (Ni₃C or Ni metal) with hydrogen uptake.

Lupu et al., 2004 b used palladium catalyzed CNFs for hydrogen adsorption.

CNFs based electrodes, grown into a porous ceramic substrate, show promising properties for applications in electrochemistry. Some aromatic compounds (hydroquinone, benzoquinone, and phenol - Murphy et al., 2003) are strongly adsorbed on the surface of carbon nanofiber composite electrode. The composite electrode has a high surface area due to the carbon nanofiber and shows promising properties for applications in electroanalysis.

Diaz et al., 2007 evaluated the performance of different nonmicroporous carbon structures (multi-wall carbon nanotubes, nanofibers, and high-surface-area graphites) as adsorbents for volatile organic compounds, hydrocarbons, cyclic, aromatic and chlorinated compounds. The evaluation was based on the adsorption isotherms, the values of heats of adsorption and values of free energy of adsorption. They observed that the adsorption of n-alkanes and

other polar probes on CNTs is less energetically favorable than the adsorption on flat graphite.

Cuervo et al., 2008 have evaluated the effect of the chemical oxidation, on the adsorption properties of CNFs. They discussed the adsorption of n-alkanes, cyclohexane and chlorinated compounds. They showed that the adsorption is a complex process, where morphological aspects are playing a key role. Both the capacity and adsorption strength decreased after the oxidative treatment of carbon nanofibers, especially in the case of chlorinated compounds. There is steric limitation in the adsorption process, after oxidation of nanofiber. In the case of aromatic compounds, the steric limitation is compensated by the interaction of aromatic rings with surface carboxylic groups. The absence of nucleophilic groups in the chlorinated compounds hinders their adsorption on the activated nanofibers.

Kovalenko et al., 2001 investigated the adsorption properties of catalytic filamentous carbon (CFC) with respect to biological adsorbates, like: L-tyrosine, bovine serum albumin, glucoamylase and non-growing bacterial cells of *Escherichia coli*, *Bacillus subtilis* and *Rhodococcus* sp. They have studied the influence of the surface chemical properties and textural parameters of CFC, on the adsorption. They used three independent methods for the calculation of the value of *accessible surface area*: comparative method, fractal method and external geometrical surface of granules. The conclusion was that the adsorption of biological adsorbates is mainly influenced by the *accessible surface area*. The roughness of the surface also affects the efficiency of the adsorption/desorption of bacterial cells.

Wei et al., 2007 presented in a review the biological properties of carbon nanotubes (the processing, chemical and physical properties, nucleic acid interactions, cell interactions and toxicological properties). The unique biological and medical properties of carbon nanostructured are of great interest in the last years. Finally, future directions in this area are discussed.

Li et al., 2005 prepared herringbone nanofibers that were subsequently oxidized, in order to create carboxylic acid groups on their surface. After that, they were functionalized with reactive linker molecules derived from diamines and triamines.

Surface functionalization is an important step to enhance wettability, dispersibility and surface reactivity of carbon nanostructures to help incorporation into composites and devices. There are two known strategies currently employed to modify carbon nanostructures surface: covalent functionalization and non-covalent wrapping of carbon nanostructures with surfactants, polymers or ceramic coatings.

The successful surface functionalization of vapour-grown carbon nanofiber materials has been extensively reported in literature. In particular, those having the platelet or herringbone structures are especially suitable for surface functionalization, due to the presence of edge-site carbon atoms.

A great advantage of carbon nanofibers is their compatibility with physiological cells and tissues; additionally, these fibers have excellent conductivity and high strength to weight ratios. The high conductivity is a promising property for electrical stimulation of neuronal cells and can be beneficial for studying the nerve functions and regeneration. The excellent electrical and mechanical properties of carbon nanofibers lead to promising potential applications as central and peripheral neural biomaterials (McKenzie et al., 2004).

Many supports as powders, beads or chips (polymers and resins, silica and silica-alumina composites and carbonaceous materials) have been studied for enzyme immobilization.

Immobilized enzymes are used as catalysts in fine chemicals and chemicals production. The immobilization of the enzymes on support brings important advantages over dissolved enzymes, e.g. the possibility of recovery and reuse, simple operation and improved stability. De Lathouder et al., 2004 functionalized ceramic monoliths with different carbon coatings and the biocatalyst (enzyme lipase) was adsorbed on the supports. They found that CNFs support have the highest adsorption capacity, preserve the activity of enzyme and have the highest stability during storage. The pore volume, surface area and the nature of surface groups of the supports influence the adsorption process of the different carbon types. To investigate the interaction between carbon nanotubes and biomolecules, Bradley et al., 2004 used compact transistor devices with carbon nanotubes being the conducting channel and studied the interaction between nanotubes and streptavidin. Olenic et al., 2009 have studied the adsorption properties of different bio-molecules onto the surface of CNFs, synthesized by CCVD method (Lupu et al 2004a). Few amino acids (alanine, aspartic acid and glutamic acid) and glucose oxidase (GOx) were adsorbed on CNFs and activated carbon (AC). Hydrophilic and hydrophobic properties of CNFs and AC surfaces were characterized by the pH value, the concentration of acidic/basic sites and by naphthalene adsorption. Carbon nanofibers with the “herringbone” structure (Figure 1) were purified in HCl. The specific area ($170\text{ m}^2\text{g}^{-1}$) was determined by BET method. The investigated carbon structures were weakly acidic mainly due to preparation and activation methods. The adsorption properties of CNFs and AC were different for various amino acids, depending on the molecular weight and acid-base functionalities of each amino acid. The interaction between GOx and CNF support was complex, depending on factors like steric hindrance or chemical groups attached to CNF surface. The filamentous morphology of CNF was responsible for the greater stability of adsorbed enzyme, compared with the enzyme used directly in solution.

| Sample | BET surface (m^2g^{-1}) | pH | Acidic values (meq g^{-1}) | Basic values (meq g^{-1}) | Naphthalene adsorption (nmol m^{-2}) |
|--------|--|------|--|---|--|
| CNFs | 170 | 6.20 | 0.15 | 0.6 | 51.17 |
| AC | 1400 | 6.52 | 0.04 | 0.28 | 27.8 |

Table 1. pH, hydrophilic and hydrophobic properties of CNFs and AC. Reprinted from ref. Olenic et al., 2009 with kind permission of Springer Science and Business Media.

The data were fitted with the Langmuir adsorption isotherm. From the adsorption isotherms (Figures 6, 7) one can see that the adsorption of amino acids onto CNFs increases from alanine to aspartic acid; when the less hydrophobic AC was used as support, the adsorption of amino acids increased from aspartic acid to alanine and to glutamic acid. Glutamic acid adsorbed on CNFs doesn't obey the Langmuir equation, due to its hydrophobicity. GOx was also adsorbed on CNF and AC. In comparison with CNF, the adsorption process on AC does not obey the Langmuir equation. This means that the intermolecular interactions between adsorbate molecules are stronger than the interaction between the adsorbate molecules and support.

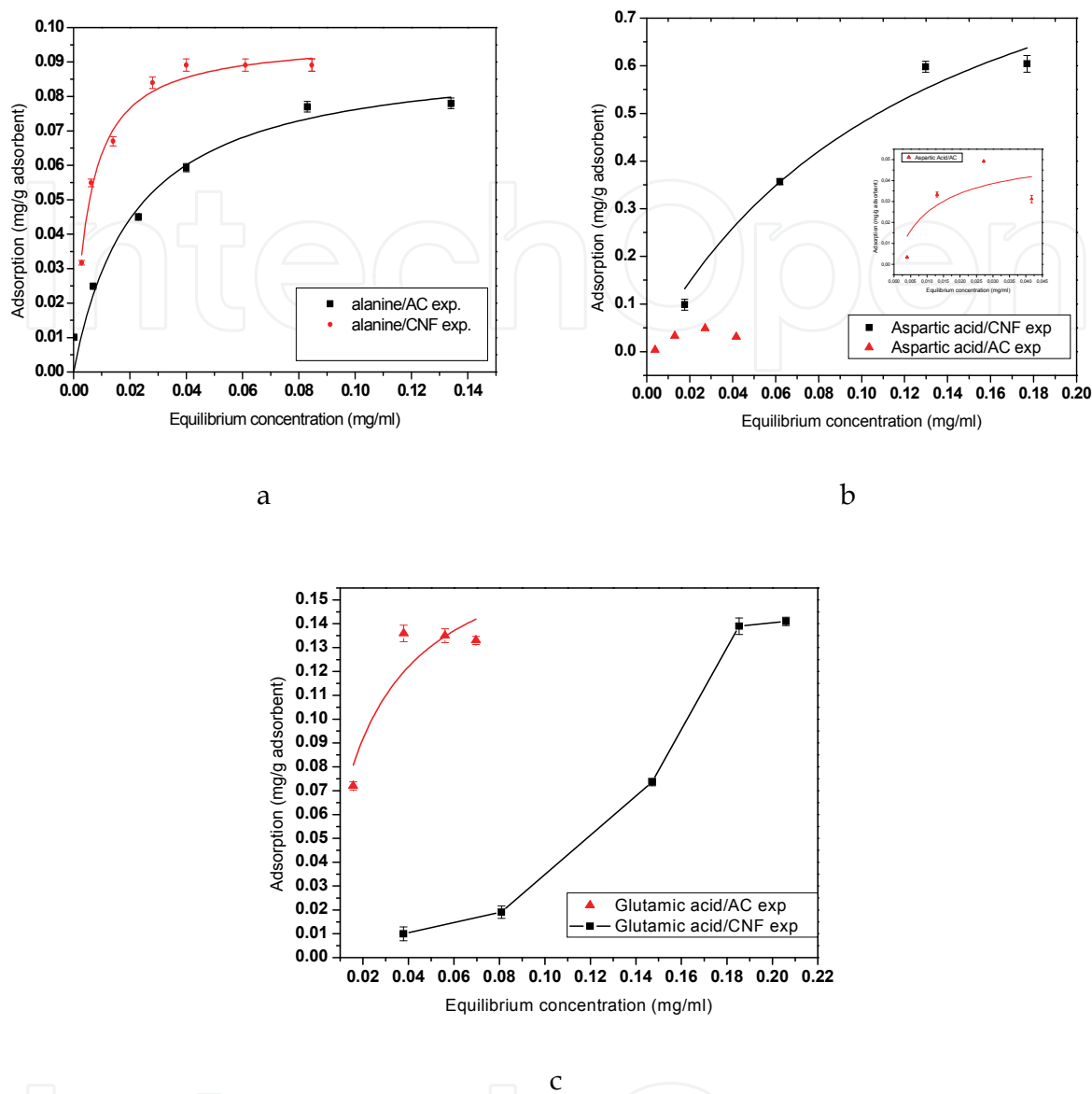


Fig. 6. The adsorption isotherms of alanine (a) aspartic acid (b) and glutamic acid (c) on CNFs and AC (error bars represent the standard deviation of the mean for 5 samples). Reprinted from ref. Olenic et al., 2009 with kind permission of Springer Science and Business Media.

Due to the fact that the *accessible surface area* (ASA) plays an important role in the adsorption of various bio-molecules, we have determined the ratio of ASA_{CNF}/ASA_{AC} by comparative method, for all adsorbate molecules. We have noticed that the adsorption of GOx on CNFs reaches saturation earlier than on AC (unpublished data).

| Bio-molecules | Alanine | Glutamic acid | Aspartic acid |
|----------------------|---------|---------------|---------------|
| ASA_{CNF}/ASA_{AC} | 1.02 | 0.027 | 5.66 |

Table 2. The ratios of ASA_{CNF}/ASA_{AC} for adsorbate molecules

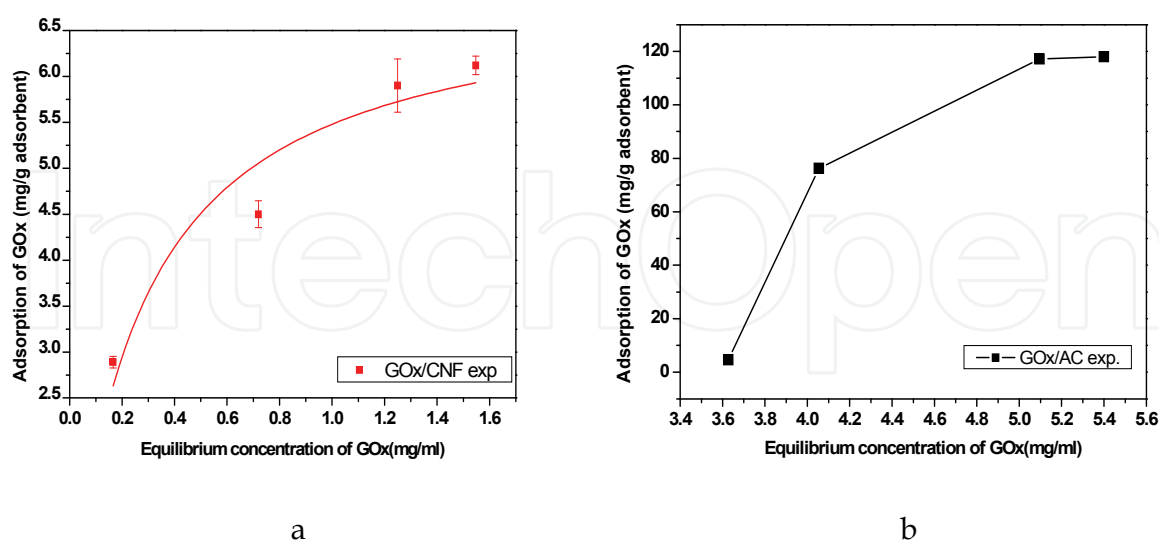


Fig. 7. The adsorption isotherms of GOx on a-CNF and b-AC (error bars represent the standard deviation of the mean for 5 samples). Reprinted from ref. Olenic et al., 2009 with kind permission of Springer Science and Business Media.

Carbon nanofibers as sensors

CNFs represent a promising material to assemble electrochemical sensors and biosensors. The direct immobilization of enzymes onto the surface of CNFs was proved to be an efficient method for the development of a new class of sensitive, stable and reproducible electrochemical biosensors. Such sensors showed good precision, high sensitivity, acceptable stability and reproducibility.

CNFs can efficiently immobilize antigen/antibody on their surfaces and can be used in the preparation of amperometric immunosensors (Wohlstadter et al., 2003; O'Connor et al., 2004; Yu et al., 2005; Viswanathan et al., 2006). An amperometric immunosensor for separation-free immunoassay of carcinoma antigen-125, based on its covalent immobilization coupled with thionine on carbon nanofiber was prepared by Wu et al., 2007. The direct electrochemistry of NADH was studied at a glassy carbon electrode modified using CNFs (Arvinte et al., 2007).

VACNFs were also used for biosensing applications (Baker et al., 2006 b). The use of highly activated CNFs for the preparation of glucose biosensors, in comparison with SWCNT and graphite powder, is presented by Vamvakaki et al., 2006. They demonstrated that CNFs are far superior to carbon nanotubes or graphite powder as matrix for the immobilization of proteins and enzymes and for the development of biosensors. They characterized the buffer capacity and the electrochemical properties of supports. Carbon nanofiber-based glucose biosensors provide higher sensitivity, reproducibility and longer lifetime. This is due to the high surface area of nanofibers which together with the large number of active sites, offers the grounds for the adsorption of enzymes. In addition, they allow for both the direct electron transfer and increased stabilization of the enzymatic activity. These carbon nanofiber materials are thus very promising substrates for the development of a series of highly stable and novel biosensors.

Metz et al., 2006 demonstrated a method for producing nanostructured metal electrodes, by functionalization of CNFs with molecular layers bearing carboxylic acid groups, which then serve as a template for electroless deposition of gold.

CNFs have been incorporated into composite electrodes for use with *liquid|liquid* redox systems (Shul et al., 2005).

CNFs are very good materials for the interface between solid state electronics and biological systems. Integrated VACNFs, grown on electronic circuits, were used in a multiplex microchip for neural electrophysiology by Nguyen-Vu et al., 2005. The chip has multiple nanoelectrode arrays with dual function: either as electrical stimulation electrodes or as electrochemical-sensing electrodes. They tested the implantable electrodes in-vitro cell culture experiments.

Lee et al., 2004 provided the fabrication of high-density arrays of biosensor elements using functionalized VACNFs (with nitro groups). The surface of VACNFs was further modified by an electrochemical reduction reaction (nitro groups on specific nanostructures were reduced to amino groups). DNA was then covalently linked to only these nanostructures. DNA-modified nanostructures have excellent biological selectivity for DNA hybridization. MWCNTs inlaid nanoelectrode array have ultrahigh sensitivity in direct electrochemical detection of guanine, in the nucleic acid target (Koehne et al., 2004).

Olenic et al., 2009 adsorbed the GOx on CNFs and prepared a glucose biosensor using potassium ferrocyanide as redox mediator (Figure 8 a). In order to detect the changes in the specific activity of GOx immobilized a long time on CNFs, an amperometric method was used in an original manner (Figure 8 b). The specific activity was determined by taking into consideration the decrease of the current in time. The proposed method is fast and very simple and demonstrates that not all the enzyme immobilized on nanofibers can catalyze the oxidation of glucose. The characteristics of biosensor are: linear range between 1.7 and 7 mM and sensitivity of 8.6 $\mu\text{A}/\text{mM}$. After 1 year, they have changed (linear range 1–3 mM and sensitivity 1.5 $\mu\text{A}/\text{mM}$).

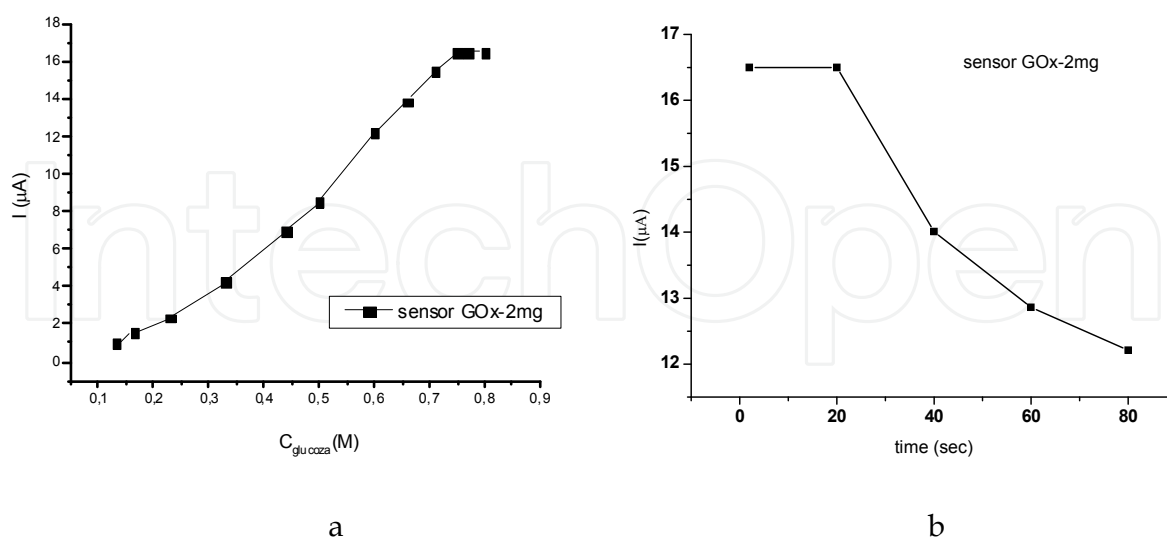


Fig. 8. a-calibration curve of glucose biosensor; b- biosensor response during glucose consumption (the points represent the media of five determinations). Reprinted from ref. Olenic et al., 2009 with kind permission of Springer Science and Business Media.

The results presented in Table 3 shows that the enzymatic activity of GOx decreases in time.

| Time | Current (μA) | Enzyme activity (U mg^{-1}) | Enzymatic activity decreased (%) |
|-------------------|------------------------------|---|-------------------------------------|
| After preparation | 96 | 157 | 0 |
| After 12 months | 38 | 64 | 59 |

Table 3. The decrease of GOx activity in time. Reprinted from ref. Olenic et al., 2009 with kind permission of Springer Science and Business Media.

We can conclude that the amount of enzyme required to prepare a high sensitive biosensor has to be larger than that adsorbed on CNFs, due to the fact that some of it does not participate to the reaction.

6. Conclusions and future research

A new synthesis technique of carbon nanofilaments in a cold wall reactor (CCVD method with inductive heating) has been achieved and improved in the laboratory where the authors are working. This method was a world premiere (Lupu et al., 2004).

Compared to the classical method, this technique is suitable for the synthesis of all types of high quality carbon nanofilaments. Its efficiency was proved by the reduction of the global synthesis time to one half and of the energetic consumption to a third. Nowadays, the method is used in many laboratories from Japan, China, USA, etc.

The obtained CNF's structures were electrochemically characterized by cyclic voltammetry. Additionally, single stranded and double stranded calf thymus DNA was physisorbed on the surface of a CNF's electrode. The oxidation peaks of adenine and guanine were recorded by differential pulse voltammetry. The authors also had in view the adsorbing properties of these nanostructures, in the presence of some biologically active substances (amino-acids and glucose oxidase). The nanomaterials have been used to obtain a glucose biosensor. A new simple and trustful method has been finalized which helps to determine the enzymatic activity of GOx. All the accomplished studies are genuine and they bring a great contibution to the literature in the field. The adsorption studies can contribute to the development of bio-technological processes, in the pharmaceutical industry and in clinical trials.

Further studies can be performed on CNFs with various morphological and structural characteristics, in order to see their influence on the adsorption and electrochemical properties. There is a possibility of enlarging the research area, by studying other biologically active substances and by simulation of their adsorption on nanostructured supports. Additionally, the study of direct oxidation (without redox mediator) of GOx and DNA on CNFs electrodes, would help in improving the construction of new types of biosensors.

Currently, the research in our laboratory is focused on the detection of new properties of the functionalized carbon nanostructures, for treatment of human and animal pancreatic cancer and other cancers in general.

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“There's Plenty of Room at the Bottom” this was the title of the lecture Prof. Richard Feynman delivered at California Institute of Technology on December 29, 1959 at the American Physical Society meeting. He considered the possibility to manipulate matter on an atomic scale. Indeed, the design and controllable synthesis of nanomaterials have attracted much attention because of their distinctive geometries and novel physical and chemical properties. For the last two decades nano-scaled materials in the form of nanofibers, nanoparticles, nanotubes, nanoclays, nanorods, nanodisks, nanoribbons, nanowhiskers etc. have been investigated with increased interest due to their enormous advantages, such as large surface area and active surface sites. Among all nanostructures, nanofibers have attracted tremendous interest in nanotechnology and biomedical engineering owing to the ease of controllable production processes, low pore size and superior mechanical properties for a range of applications in diverse areas such as catalysis, sensors, medicine, pharmacy, drug delivery, tissue engineering, filtration, textile, adhesive, aerospace, capacitors, transistors, battery separators, energy storage, fuel cells, information technology, photonic structures and flat panel displays, just to mention a few. Nanofibers are continuous filaments of generally less than about 1000 nm diameters. Nanofibers of a variety of cellulose and non-cellulose based materials can be produced by a variety of techniques such as phase separation, self assembly, drawing, melt fibrillation, template synthesis, electro-spinning, and solution spinning. They reduce the handling problems mostly associated with the nanoparticles. Nanoparticles can agglomerate and form clusters, whereas nanofibers form a mesh that stays intact even after regeneration. The present book is a result of contributions of experts from international scientific community working in different areas and types of nanofibers. The book thoroughly covers latest topics on different varieties of nanofibers. It provides an up-to-date insightful coverage to the synthesis, characterization, functional properties and potential device applications of nanofibers in specialized areas. We hope that this book will prove to be timely and thought provoking and will serve as a valuable reference for researchers working in different areas of nanofibers. Special thanks goes to the authors for their valuable contributions.

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